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May 12, 2004

International Pyrotechnics Seminar  
Fort Collins, CO, United States  
July 12, 2004 through July 16, 2004

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*Proceedings of the 31<sup>st</sup> International Pyrotechnics Seminar*

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Energetic Materials**

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**UCRL–PROC–204118**

# Synthesis and Characterization of Mixed Metal Oxide Nanocomposite Energetic Materials

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## ABSTRACT

In the field of composite energetic materials, properties such as ingredient distribution, particle size, and morphology affect both sensitivity and performance. Since the reaction kinetics of composite energetic materials are typically controlled by the mass transport rates between reactants, one would anticipate new and potentially exceptional performance from energetic nanocomposites. We have developed a new method of making nanostructured energetic materials, specifically explosives, propellants, and pyrotechnics, using sol-gel chemistry. A novel sol-gel approach has proven successful in preparing metal oxide/silicon oxide nanocomposites in which the metal oxide is the major component. By introducing a fuel metal, such as aluminum, into the metal oxide/silicon oxide matrix, energetic materials based on thermite reactions can be fabricated. Two of the metal oxides are tungsten trioxide and iron(III) oxide, both of which are of interest in the field of energetic materials. In addition, due to the large availability of organically functionalized silanes, the silicon oxide phase can be used as a unique way of introducing organic additives into the bulk metal oxide materials. These organic additives can cause the generation of gas upon ignition of the materials, therefore resulting in a composite material that can perform pressure/volume work. Furthermore, the desired organic functionality is well dispersed throughout the composite material on the nanoscale with the other components, and is therefore subject to the same increased reaction kinetics. The resulting nanoscale distribution of all the ingredients displays energetic properties not seen in its microscale counterparts due to the expected increase of mass transport rates between the reactants. The synthesis and characterization of iron(III) oxide/organosilicon oxide nanocomposites and their performance as energetic materials will be discussed.

## INTRODUCTION

Since the invention of black powder, one thousand years ago, the technology for making solid energetic materials has remained either the physical mixing of solid oxidizers and fuels (e.g. black powder), or the incorporation of oxidizing and fuel moieties into one molecule (e.g., trinitrotoluene (TNT)). The basic distinctions between these energetic composites and energetic materials made from monomolecular approaches are as follows. In composite systems, desired energy properties

can be attained through readily varied ratios of oxidizer and fuels. A complete balance between the oxidizer and fuel may be reached to maximize energy density. However, due to the granular nature of composite energetic materials, reaction kinetics are typically controlled by the mass transport rates between reactants. Hence, although composites may have extreme energy densities, the release rate of that energy is below that which may be attained in a chemical kinetics controlled process. In monomolecular energetic materials the rate of energy release is primarily controlled by chemical kinetics, and

not by mass transport. Therefore, monomolecular materials can have much greater power than composite energetic materials. A major limitation with these materials is the total energy density achievable. Therefore, it is desirable to combine the excellent thermodynamics of composite energetic materials with the rapid kinetics of the monomolecular energetic materials. One possible way to do this is to mix the components of composite energetic materials on a size scale which will limit the effects of mass transport on the reactants, thus providing kinetics similar to those obtained in monomolecular energetic materials.

We have previously prepared pyrotechnic and explosive composites based on thermite reactions whose fuel and oxidizer constituents are intimately mixed on the nanometer-sized scale [1-2]. These energetic nanocomposites, in an attempt to prepare a high energy, high power energetic nanocomposite as discussed above, are prepared by taking advantage of the unique nano-architecture and mixing properties provided by sol-gel chemistry. One limitation inherent in any thermite energetic, however, is the inability of the energetic material to do pressure/ volume-work on an object. Thermites release energy in the form of heat and light, but are unable to move objects. Typically, work can be done by a rapidly produced gas that is released during the energetic reaction. In the case of the thermite energetic composite, a “gas generator” can be added to the composite mixture, however, this additive will be subject to the same mass transport issues mentioned above.

This paper will discuss the preparation of energetic nanocomposites containing organically modified iron(III) oxide-silica oxidizing phases. All nanocomposites have been synthesized using sol-gel chemistry in which aluminum metal particles are intimately mixed with the iron(III) oxide-silicon oxide phase. The incorporation of organic functionality through the silicon oxide

precursors results in the intimate mixing of a gas generator into the energetic composite on the nanoscale. The release of gas upon ignition of the nanocomposite material is observed.

## EXPERIMENTAL DETAILS

### Synthesis of organic functionalized mixed metal oxide energetic nanocomposites

In a typical reaction,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.84 g, 3 mmol) was dissolved with stirring in 3.8 g of 200 proof ethanol in a polyethylene vial to give a yellow-brown solution. Once the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved, the desired amount of organosilane (Fe/Si atomic molar ratio of 3-5) was added to the solution and the resulting mixture was allowed to stir for 10 minutes. To induce gelation, a proton scavenging organic epoxide, propylene oxide (PO; 28 mmol), was then added to the sol in at least two separate aliquots. (**CAUTION:** addition of PO to a  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution is accompanied by significant heat generation, which in some cases leads to flash boiling of the synthesis solution. This reaction should only be performed in a well ventilated lab space with the careful addition of PO to the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /organosilane solution in two or three aliquots, allowing for sufficient cooling time between additions.) Before the addition of the last aliquot of epoxide, 2  $\mu\text{m}$  aluminum metal (6 mmol; Al/Fe=0.5) was added to the sol and the mixture stirred for 15 minutes to ensure thorough mixing. While continuing to gently stir, the final aliquot of PO was added and the sol allowed to gel.

Samples containing 40 nm diameter sized aluminum particles were prepared by solution methods. The desired ratio of sol-gel prepared oxidizer to nanometer aluminum (Nanotechnologies, Inc.) was slurried in hexane to achieve a high degree of mixing. Following mixing, the hexane was allowed to evaporate on a hot plate, leaving behind the mixed energetic nanocomposite.

## Processing of organic/inorganic hybrid gels

All gels remained covered and were aged for at least 48 hours after the initial gelation. Following aging, each gel was subjected to a pore-washing/solvent exchange step in 200-proof ethanol for 3 – 5 days. During this time, the wash solution was replaced at least three times with fresh ethanol. For xerogel preparation, following ethanol washing, the alcogels were solvent exchanged with *n*-pentane and were then dried ambiently for 2-3 days. For aerogel preparation, the solvent-exchanged gels were processed in a Polaron™ supercritical point dryer. The ethanol in the wet-gel pores was exchanged for CO<sub>2</sub>(*l*) for 3 – 4 days at ~12 °C, after which the temperature of the vessel was ramped to ~45 °C while maintaining a pressure of ~100 bar. The vessel was then depressurized at a rate of about 7 bar/hr.

Following the initial drying step (ambient or supercritical), all gel materials were further processed in a vacuum oven (–60 torr) at 85 °C for 24 hours to complete the drying process. The resulting materials were then ground to fine powders using a mortar and pestle as appropriate.

## Physical characterization of nanocomposites

Prior to taking FTIR spectra, samples were prepared by grinding together in a 1:100 weight ratio the Fe-Si mixed oxide material and dry potassium bromide, respectively, followed by pressing of the mixture into a transparent pellet. All FTIR was performed under a nitrogen purge on a ThermoNicolet Nexus 4000 spectrometer in transmission mode at 4 cm<sup>–1</sup> resolution for 128 scans.

Transmission electron microscopy (TEM) was performed on a Philips CM300FEG operating at 300 keV using zero loss energy filtering with a Gatan energy imaging filter (GIF) to remove inelastic scattering. The images were taken under bright field conditions and slightly defocused to increase contrast. The

images were also recorded on a 2K × 2K CCD camera attached to the GIF.

Energy filtered TEM (EFTEM) element maps were obtained by electron energy loss spectroscopy (EELS) in tandem with the Philips CM300FEG TEM microscope. All EELS measurements were made with a Gatan model 607 electron energy-loss spectrometer attached to the microscope and were made at the Si-L<sub>2,3</sub> and F-K edges. Images were processed using Digital Micrograph™ 3.3.1 software from Gatan, Inc.

Scanning electron microscopy (SEM) was carried out using a Hitachi S-4500 cold field emission microscope. Typical accelerating voltages used ranged from 1.8 to 6 kV and depended on sample conductivity.

## DISCUSSION

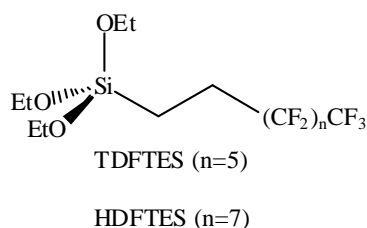
### Synthesis and characterization of energetic nanocomposites

We have previously reported the formulation of Fe-oxide/Al energetic nanocomposites via an *in situ* sol-gel synthesis of the Fe-oxide oxidizing phase that encapsulates aluminum fuel particles [1-2]. The starting materials are simple, inexpensive metal salts, primarily FeCl<sub>3</sub>·6H<sub>2</sub>O, either nano- or micron-grained aluminum particles, and an organic epoxide that initiates Fe-oxide formation through the establishment of a uniform pH gradient in the synthesis solution [3-5].

We have recently expanded this epoxide addition method to the synthesis of Fe-Si mixed oxide composites. Addition of either TMOS or TEOS to the reaction described above resulted in the first examples of Fe-Si mixed oxide nanocomposites in which iron(III) oxide is the major component [6]. This technique has now been expanded to the synthesis of organic/inorganic composite energetic materials by using a variety of organically functionalized silsesquioxanes. The resulting materials are organic/inorganic hybrid composites in which all

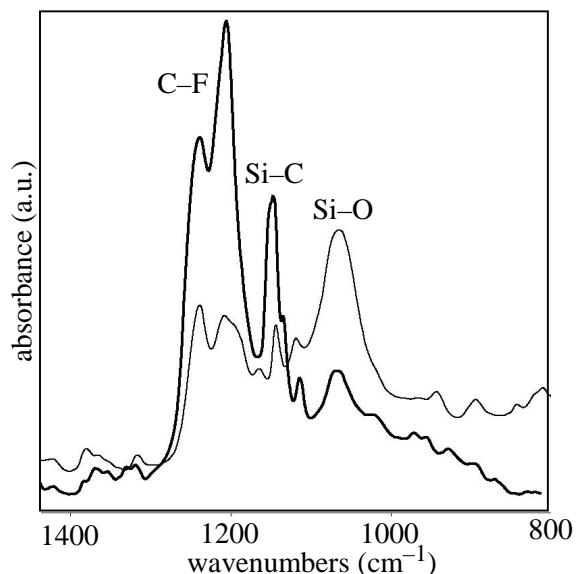
the components are well dispersed throughout the bulk material [7].

The organic functionality chosen for these materials was comprised of a variety of fluoroalkanes due to the energetic redox reaction between aluminum metal and  $\text{CF}_2$  moieties [2]. Fluoroalkane functionality was incorporated into the energetic composites through the Si-oxide phase by using silsesquioxanes, which contain fluoroalkane functionality, as starting materials. The two silsesquioxanes investigated were the commercially available (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (TDFTES) and (heptadeca-fluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (HDFTES), and are shown below.



Infrared (IR) spectra of the resulting inorganic/organic composites show the successful incorporation of the fluoroalkane into the hybrid materials, as can be seen in Figure 1. The vibrational bands for Si-O ( $1060\text{ cm}^{-1}$ ), Si-C ( $1150\text{ cm}^{-1}$ ), and C-F ( $1200\text{--}1250\text{ cm}^{-1}$ ) confirm the presence of the fluoroalkane functionality in the final composite materials. Though the IR spectra of the composites confirm the presence of the Si-oxide and organics, it provides no information as to the distribution and degree of mixing of the constituents in the hybrid composite.

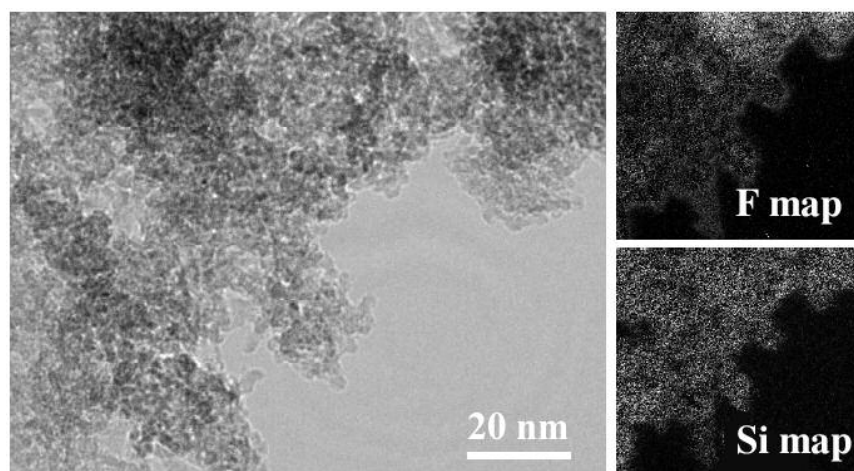
The degree of dispersion between the phases throughout the bulk material is of interest in any composite material, but is especially important for the nanostructured energetic materials due to the effect of mass transport on the reaction kinetics. The nanostructure of the organic functionalized metal oxide materials was characterized by TEM and EFTEM to determine the degree of dispersion of the organosilica phase in the material. Figure 2 contains TEM



**Figure 1.** IR spectra of Fe-Si mixed oxide organic/inorganic composites made with TDFTES (thin line; Fe/Si=4) and HDFTES (bold line; Fe/Si=3).

images of a Fe/Si=5 (mol/mol) aerogel made with the silica precursor HDFTES. The material is a collection of nanoparticles interconnected to form a mesoporous structure. The size of the particles appears to be fairly uniform throughout the gel, with particles sizes ranging from 2-5 nm in diameter. No evidence of phase separation between Fe and Si-oxides is apparent from TEM analysis or EFTEM analysis. As a result, dispersion of the organosilica phase appears to be uniform throughout the material on the nanoscale, as can be seen from the fluorine and silicon element maps in Figure 2. In fact comparison of individual particles between the TEM bright field image and EFTEM images shows there to be a mix of both organosilica and iron(III) oxide in a significant number of particles.

Incorporation of aluminum metal into the organically functionalized oxide matrix is accomplished through gelation of the matrix around the aluminum particles. The aluminum used in these studies was comprised of  $2\text{ }\mu\text{m}$  aluminum particles introduced into the sol just prior to gelation. Figure 3 shows an SEM of the



**Figure 2.** TEM micrograph of a Fe/Si=5 organic/inorganic aerogel composite. Fluorine and silicon element maps show the dispersion of the organosilica phase throughout the material.

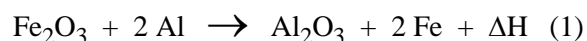
final energetic composite. The Al metal particles are completely coated by the oxidizing matrix, thus showing the degree of mixing achievable for these energetic composite materials.

Similar composite materials were also made with the incorporation of 40 nm diameter aluminum particles. These materials were mixed using solvent techniques following the sol-gel preparation of the Fe oxide/organosilica phase. Thorough mixing of the two nanoparticulate phases was achieved and phenome-

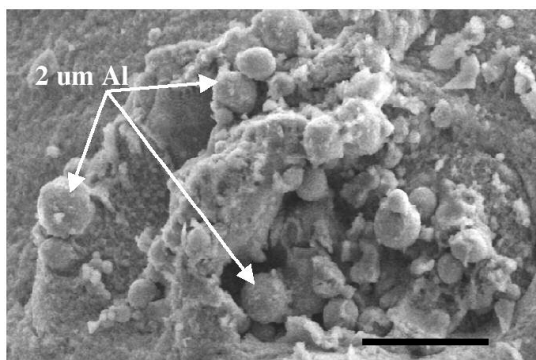
nological burn properties for both micron sized Al and nanometer-sized Al energetic composites is discussed below.

### Phenomenological burn properties

The traditional redox reaction between iron(III) oxide and aluminum metal for a thermite composite energetic material is shown below in Equation 1. For this reaction, energy is



released in the form of heat and light, however, there is no gas produced upon ignition of the thermite. By incorporating organic additives, a thermite can be prepared that will generate gas upon ignition of the energetic composite [2]. A proposed reaction for the iron(III) oxide/aluminum metal/fluoroorganic composites synthesized in this study is shown below in Equation 2. As can be seen, gas from the



**Figure 3.** SEM images of a Fe/Si=5 organic/inorganic energetic nanocomposite with 2 μm Al metal particles. The black bar indicates 5 μm.



decomposition of the organic additives is generated, thereby resulting in an energetic composite material that has the potential to perform pressure/volume (PV) work.

Phenomenological burn observations indicate that the organic functionalized Fe/Si mixed oxide nanocomposites burn very rapidly and violently, essentially to completion, with the generation of significant amounts of gas. Figure 4 (top) shows a comparison of the ignition of an energetic nanocomposite with and without organic functionalization. The still image of the energetic nanocomposite without organic functionalization exhibits rapid ignition and emission of light and heat. The still image of the energetic nanocomposite with organic

functionalization also exhibits these characteristics, but it also exhibits hot particle ejection due to the production of gas upon ignition. This reaction is very exothermic and results in the production of very high temperatures, intense light, and pressure from the generation of the gaseous byproducts resulting from the decomposition of the organic moieties.

These materials were also mixed with nanometer aluminum. Figure 4 (bottom) shows a still image of the ignition of a fluoroorganic functionalized composite mixed with 40 nm aluminum. This composite is much more reactive than the same oxidizing phase mixed with 2  $\mu\text{m}$  aluminum metal. As can be seen in



**Figure 4.** Still images of thermal ignition of samples of iron(III) oxide/2  $\mu\text{m}$  Al (left), fluoroorganic/Fe-oxide/2  $\mu\text{m}$  Al (right), and fluoroorganic/Fe-oxide/40 nm Al (bottom) energetic nanocomposites.

Figure 4, the burning of the composite with 40 nm aluminum occurs much too quickly to be able to observe the hot particle ejection displayed by the slower burning composite made with 2  $\mu\text{m}$  aluminum. This observation is a good example of the importance mixing and the scale of the reactants can have on the physical properties of the final energetic composite material. When the degree of mixing is on the nano-scale, the material is observed to react much more quickly, presumably due to the increase in mass transport rates of the reactants, as discussed above.

It should be noted that these composites also contain a silicon oxide phase ( $\text{SiO}_{3/2}$ ). For the purpose of the phenomenological burn comparisons between the materials presented here, it is assumed that the silicon oxide phase does not participate in the energetic reactions proposed for these materials. This notion is supported by the large reduction potential of silicon oxide, making it difficult for such an oxide phase to undergo an exothermic redox reaction. As such, we believe that in the extreme reaction conditions for ignition of these materials in air that the silicon oxide phase is instead completely oxidized to  $\text{SiO}_2$ , an observation supported by the present of charred solids following the burning of these materials. For purposes of the discussion here, we have not considered the reaction of the silicon oxide phase in the overall proposed reaction presented in Equation 2. Since the silicon oxide almost certainly affects the performance of these materials, studies are currently being performed to determine the role the silicon oxide phase plays during burning. Furthermore, the reaction products from the burning of these composites are being characterized to further elucidate the exact reaction products (*i.e.* gases, charred solids, etc.) that are being produced during the burning of these composite materials.

## CONCLUSIONS

We have successfully synthesized energetic nanocomposites using sol-gel methodology that incorporate gas generators through an organic functionalized iron(III) oxide-silica oxidizing phase. The energetic materials display an intimate mixing on the nano-scale of all components. The material is exothermic when ignited, displaying hot particle ejection caused by the rapid generation of gas from decomposition of the organic functionality.

As is the case with most nano-scale materials systems, the energetic nanocomposites in this study were observed to have different properties as compared to their traditionally prepared micron-scale counterparts. Future work will focus on characterization of the products and measurement of burn rates, temperatures, and pressures generated by such materials. Such studies will continue to elucidate the influence that nano-scaled materials will have in the field of energetic composites. These energetic nanocomposites have potential applications as pyrotechnics and propellants.

## ACKNOWLEDGEMENTS

This Work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. The authors would like to thank Jennifer S. Harper for TEM images and Jim Ferreira for SEM images.

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